# <Division of Materials Chemistry> Chemistry of Polymer Materials

# Division of Materials Chemistry
## - Chemistry of Polymer Materials -

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Prof
TSUJII, Yoshinobu
(D Eng)

Assist Prof
OHNO, Kohji
(D Eng)

Assist Prof
GOTO, Atsushi
(D Eng)

PD
KIM, Jeong Sik
(D Eng)

Proj Res
SHINJO, Ayaka

### Students

OKAYASU, Kenji (D3)
NOMURA, Akihiro (D1)
KAYAMA, Yuzo (M2)
NAGASAWA, Koji (M2)
YOSHIOKA, Yuu (M2)
AKASHI, Tatsuki (M1)
HSU, Sho Yao (M1)
HUANG, Yun (RS)
NAKAHARA, Ryo (UG)
TAKATA, Akisato (UG)
SHINMURA, Masahito (UG)

### Visitors

| | |
|---|---|
| Prof WATANABE, Junji | Tokyo Institute of Technology, 4 April 2008 |
| Mr BOMPART, Mark | Compiegne University of Technology, France, 24 June–19 August 2008 |
| Prof HAUPT, Karsten | Compiegne University of Technology, France, 6 September 2008 |
| Prof KITAOKA, Takuya | Kyushu University, 18 December 2008 |
| Prof FUJIKAWA, Seizo | Hokkaido Univesity, 19 December 2008 |

## Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

## Research Activities (Year 2008)

### Publications

Arita T, Kayama Y, Ohno K, Tsujii Y, Fukuda T: High-Pressure Atom Transfer Radical Polymerization of Methyl Methacrylate for Well-Defined Ultrahigh Molecular-Weight Polymers, *Polymer*, **49**, 2426-2429 (2008).

Morinaga T, Ohno K, Tsujii Y, Fukuda T: Structural Analysis of Semisoft Colloidal Crystal by Confocal Laser Scanning Microscopy, *Macromolecules*, **41**, 3620-3626 (2008).

Goto A, Tsujii Y, Fukuda T: Reversible Chain Transfer Catalyzed Polymerization (RTCP): A New Class of Living Radical Polymerization, *Polymer*, **49**, 5177-5184 (2008) (Feature Article).

### Presentations

Tsujii Y, Novel Properties of CPBs. Int. Conf. Adv. Func. Polym. Self-Org. Mater. (IC-PSM 2008), Busan, Korea, 22–26 September 2008.

8 Presentations, 57th Spring Meeting, Soc. Polym. Sci., Jpn., Yokohama, 28–30 May 2008.

5 Presentations, 57th Autumn Meeting, Soc. Polym. Sci., Jpn., Osaka, 24–26 September 2008.

### Grants

Fukuda T, Science and Technology of CPB, Grant-in-Aid for Specially Promoted Research, 1 April 2005–31 March 2009.

Tsujii Y, Creation of New Bio-Interfaces Based on CPB, Grant-in-Aid for Science Research (A), 1 April 2005–31 March 2008.

Tsujii Y, Development of Novel Lithium Ion Battery with Network Channel of High Ionic-Conductivity,

## High-Pressure Atom Transfer Radical Polymerization of Methyl Methacrylate for Well-Defined Ultrahigh Molecular-Weight Polymers

The feasibility of high-pressure atom transfer radical polymerization (ATRP) for synthesizing well-defined polymers of extraordinarily high molecular weights was demonstrated. ATRP of methyl methacrylate (MMA) under pressures up to 500 MPa was investigated at 60°C. The addition of a small amount of a $Cu(II)Cl_2$/ligand complex along with the general benefits of high pressure of enhancing propagation and suppressing termination brought about an excellent control of polymerization even with an extremely low concentration of ATRP initiator. For example, there was produced PMMA with a number-average molecular weight $M_n$ of $3.6 \times 10^6$ and a polydispersity index ($M_w/M_n$) of 1.24, which has never been achieved by conventional ATRP.

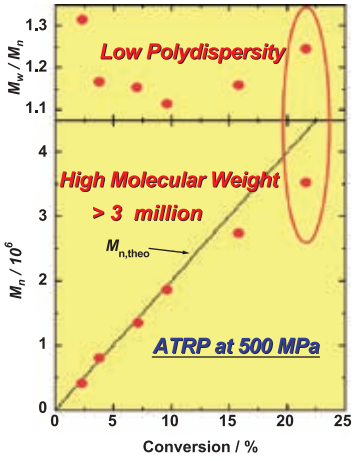


**Figure 1.** Plot of $M_n$ and $M_w/M_n$ vs monomer conversion for the ATRP of MMA at 500 MPa.

## Alcohols as a Novel Class of Catalysts for a Living Radical Polymerization

Alcohols (phenols and a vinyl alcohol) were successfully used as a novel class of catalysts for a living radical polymerization (RTCP). Low-polydispersity polystyrenes and polymethacrylates with predicted molecular weight were obtained with a fairly high conversion in a fairly short time. Notably, the alcohols include common antioxidants for foods and resins (e.g., BHT), phenol itself, and even natural compounds (e.g., vitamins). Their commonness and environmental safety may be attractive for practical applications.

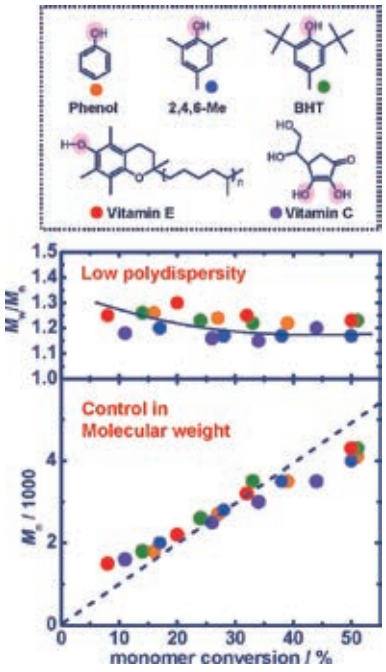


**Figure 2.** Plots of molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) vs monomer conversion for the polymerizations of styrene with alcohols (catalysts).

Development of High-Performance Battery System for Next-Generation Vehicles by NEDO, 1 July 2007–20 March 2008.

Tsujii Y, R&D of High-Efficient Organic Thin-Film Solar Cell with Supra-Hierarchical Nano-Structure, R&D for Next Generation PV System Technologies by NEDO, 1 September 2006–20 March 2010.

Ohno K, Science of Semi-Soft Colloidal Crystals, Grant-in-Aid for Young Scientists (A), 1 April 2005–31 March 2008.

Goto A, Non-Transition-Metal Catalyzed and Photo-Induced LRPs, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Goto A, Development of Green LRP with Low Cost, Industrial Technology Research Grant Program by NEDO, 10 September 2007–31 August 2011.

Goto A, Fundamentals and Applications of Non-Transition-Metal Catalyzed LRP, Mitsubishi Chemical Corporation Fund, 1 November 2007–31 August 2008.

Goto A, Development of New LRP, JST Promotion of Technology Research Partnership, 10 August 2008–31 July 2009.

## Award

Goto A, Young Scientist Presentation Award, 54th Annual Kobe Polymer Research Symposium, 18 July 2008.